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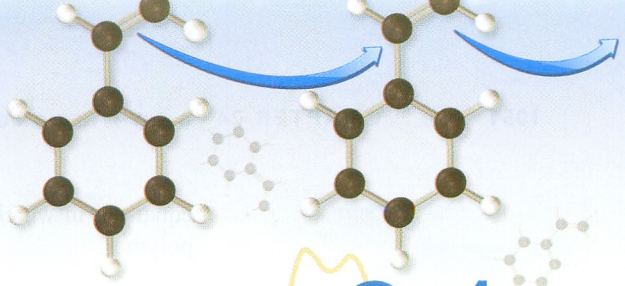

Synthetic Polymers

CHAPTER 24

MASTERING ORGANIC CHEMISTRY

- Identifying the Repeat Unit for Any Addition or Condensation Polymer
- Understanding the Mechanisms for the Formation of Addition Polymers
- Understanding the Structure and Stereochemistry of Polymers
- Understanding How the Structure of a Polymer Affects Its Physical Properties
- Understanding the Chemical Properties of a Polymer

POLYMERS ARE VERY large molecules made up of repeating units. A majority of the compounds produced by the chemical industry are ultimately used to prepare polymers. These human-made or synthetic polymers are the plastics (polyethylene, polystyrene), the adhesives (epoxy glue), the paints (acrylics), and the fibers (polyester, nylon) that we encounter many times each day. It is difficult to picture our lives without these materials. In addition to these synthetic polymers, natural polymers such as wood, rubber, cotton, and wool are all around us. And, of course, life itself depends on polymers such as carbohydrates, proteins, and DNA. This chapter discusses synthetic polymers. Naturally occurring polymers are presented in Chapters 25, 26, and 27.

First, a common method of forming polymers by a radical reaction is discussed. After the structures of the addition polymers made by this method are examined, several other procedures that can be used to prepare these or similar polymers are presented. Next, the effect of the structure of a polymer on its physical properties is discussed. This provides a basis for understanding the properties and uses of a number of other addition polymers. Rubbers (elastomers) are then discussed, followed by condensation polymers and thermosetting polymers. The chapter concludes with a brief examination of the chemical properties of polymers.

24.1 RADICAL CHAIN POLYMERIZATION

Polymers can be considered to be formed from the bonding of a large number of individual units, called monomers. This can be represented by the following general

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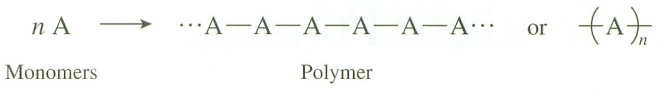
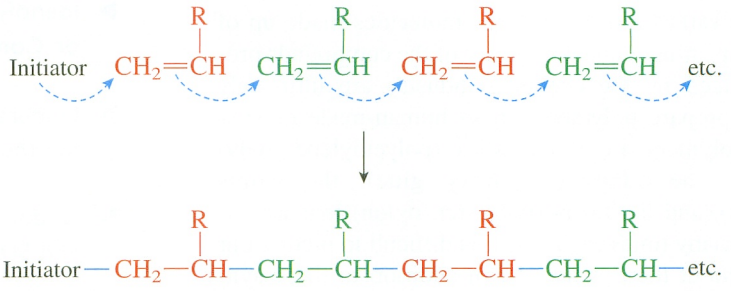
equation, in which some large number (n) of monomers (A) are combined to form a polymer:

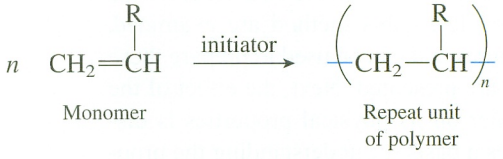


Because the number of monomers that combines to form an individual polymer molecule is usually very large—hundreds or even thousands—polymers are extremely large and are termed **macromolecules.**

Polymers are often classified as **addition polymers** or **condensation polymers** according to the general mechanism by which they are prepared. Most addition polymers are prepared by the reaction of an alkene monomer as illustrated in the following equation:

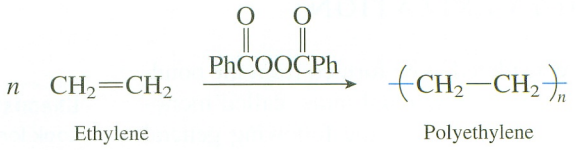


In this process, some initiator molecule adds to one carbon of the CC double bond of the monomer to generate a reactive site, such as a radical or a carbocation, at the other carbon. This reactive carbon species then adds to another monomer to produce another reactive carbon species, and the process continues until a large number of monomers have been connected. Another way to represent this reaction shows the repeating unit that is formed when the monomers react to give the polymer:



These addition polymers are often called **vinyl polymers** because of the vinyl group that is present in the monomers.

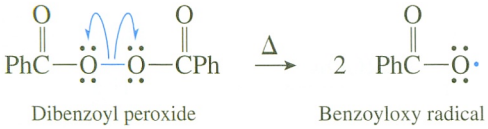
Although several variations occur, depending on the reactive intermediate that is present, all addition polymers are formed by chain mechanisms, in which one initiator molecule causes a large number of monomers to react to form one polymer molecule. For this reason these polymers are also known as **chain-growth polymers.** To better understand how this process occurs, let's examine a specific case, the formation of polyethylene by a radical chain mechanism, as shown in the following equation:

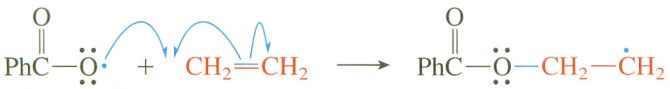


As is the case with other reactions that proceed by a radical chain mechanism (see Chapter 21), this reaction involves three kinds of steps: initiation, propagation, and termination.

Initiation

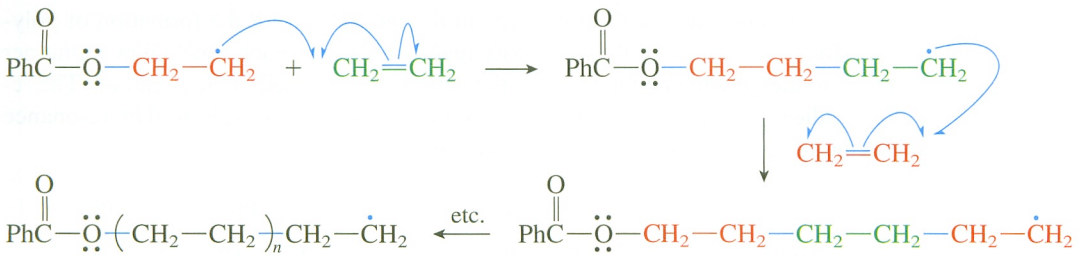
Recall that the initiation step generates the radicals. In this case the weak oxygen–oxygen bond of the initiator, dibenzoyl peroxide, cleaves to produce two benzoyloxy radicals. A benzoyloxy radical then adds to the CC double bond of an ethylene molecule:





Propagation

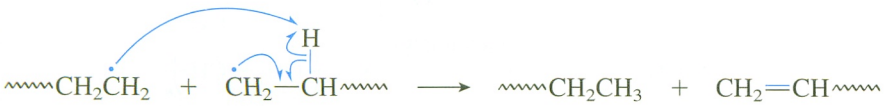
In the propagation steps a carbon radical adds to the double bond of a monomer to produce a larger carbon radical. This radical adds to another ethylene to produce an even larger radical, and the process continues until the radical is somehow destroyed.



Termination

Various types of termination reactions can occur. Two radicals can couple to form non-radical products:

Or one radical can abstract a hydrogen from the carbon adjacent to the radical center of another radical in a disproportionation process:

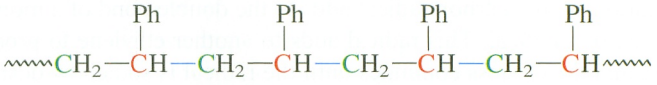


The average length of the polymer depends on the average number of propagation cycles that occur before a termination occurs. As is the case with many radical chain reactions, terminations are relatively rare because the concentration of radicals is extremely low. Therefore, the probability of one radical encountering another is also quite low. This means that a typical polymer molecule is composed of thousands of monomers. For a hydrocarbon polymer such as polyethylene, useful mechanical properties are not present until the polymer contains more than approximately 100 monomer units.

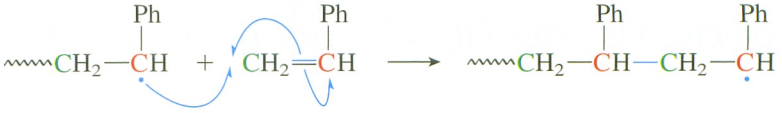
Another polymer that can be produced by radical chain polymerization is polystyrene:

Styrene Polystyrene

In this case the two carbons of the double bond of the monomer are not identical. The polymer is found to have a regular structure in which the α-carbon of one monomer is always bonded to the β-carbon of the next, as shown in the following partial structure for polystyrene. The polymer is said to be formed by head-to-tail bonding of the monomer units.



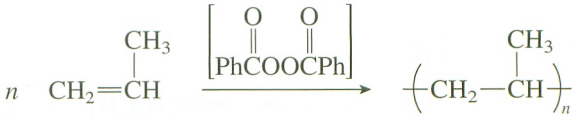
Examination of the propagation steps in the mechanism for the formation of polystyrene makes the cause of this regularity readily apparent. Each time a new monomer is added to the growing polymer chain, the new bond is formed to the β-carbon. The resulting radical, with the odd electron located on the α-carbon, is stabilized by resonance involving the phenyl group and the odd electron:



As was the case with the radical addition reactions discussed in Chapter 21, the addition always occurs so as to produce the more stable radical. Because most other substituents also stabilize a radical on the carbon to which they are attached, vinyl polymers typically result from head-to-tail coupling of their monomer units.

PROBLEM 24.1

Show all of the steps in the mechanism for the radical polymerization of propylene and explain why the polymer is formed by head-to-tail bonding of the monomer units.



PROBLEM 24.2

Show the repeat unit of the polymers that would result from addition polymerization of these monomers:

a) $CH_2{=}CHCl$ Vinyl chloride

b) $CH_2{=}CHC{\equiv}N$ Acrylonitrile

c) $CH_2{=}CCl_2$ Vinylidene chloride

PROBLEM 24.3

Show the monomers that could be used to prepare these polymers:

a) $-(CH_2-CH(OCCH_3))_n-$ Poly(vinyl acetate)

b) $-(CF_2-CF_2)_n-$ Teflon

24.2 STRUCTURES OF POLYMERS

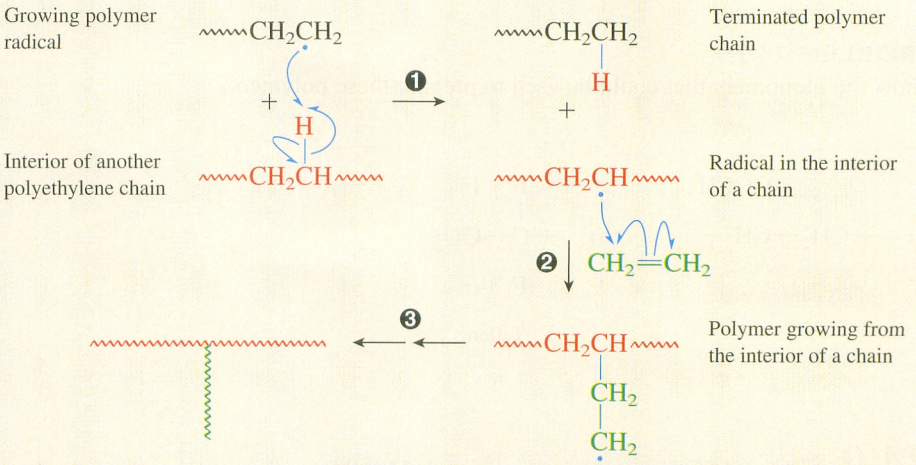
Let's consider the structure of polyethylene in more detail. First, it is important to note that the number of monomers varies widely from one macromolecule to another. The termination steps, which stop the growth of individual polymer chains, occur at random times during the polymerization of those chains. Thus, one reacting chain may terminate early, resulting in a polymer molecule that contains relatively few monomer units, whereas another may terminate much later in the chain process, resulting in a molecule that contains many more monomer units. Although it is possible to exercise some experimental control over the average molecular mass of the polymer—that is, the average number of monomer units in each macromolecule—all synthetic polymers are composed of a variety of individual macromolecules of differing molecular masses.

The structure at one end of a polymer chain depends on the initiator that started that particular chain, and the structure at the other end depends on how that chain terminated. However, most polymers are so large that the ends do not have much effect on their properties. Therefore, the structure of a polymer is usually represented by its repeat unit, and the ends are not specified.

The radical chain mechanism shown in Section 24.1 implies that polyethylene and polystyrene are composed of linear macromolecules—that is, that the carbons of the vinyl groups of the monomers are connected in a straight chain. In fact, two processes can cause individual macromolecules to have branched structures. The first of these occurs when a growing radical chain abstracts a hydrogen from a random position in the interior of another macromolecule. This process, called chain transfer, occurs when the radical does not find another monomer unit to which to add nor another radical

❶ The radical end of a growing polymer chain may occasionally abstract a hydrogen from the interior of another chain. This process is favorable because a primary radical in the reactant is converted to a secondary radical in the product. This terminates the original polymer and forms a reactive radical in the interior of the second chain that can serve as a site to initiate polymerization.

❷ The new radical can add to an ethylene monomer, resulting in a polymer chain growing from the interior of this macromolecule. Although a secondary radical is converted to a primary radical, this step is still exothermic because a weak pi bond is broken and a stronger sigma bond is formed.


Growing polymer radical
Terminated polymer chain
Interior of another polyethylene chain
Radical in the interior of a chain
Polymer growing from the interior of a chain

❸ This process results in the formation of a long branch on the original polymer chain. This is represented schematically by the structure at the left.

Figure 24.1

MECHANISM OF THE FORMATION OF A LONG BRANCH IN THE RADICAL POLYMERIZATION OF ETHYLENE.

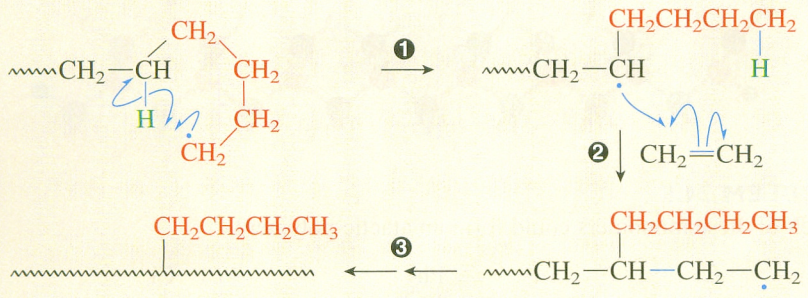
center so that termination can occur. Chain transfer results in the termination of the original chain but forms a new radical in the interior of the other macromolecule. Polymerization can occur at this new radical site, resulting in the formation of a long branch on the macromolecule. The formation of such a long branch in polyethylene is outlined in Figure 24.1.

A second process results in the formation of shorter branches that contain only four carbons. These result when the radical end of a growing polymer chain reaches back and abstracts a hydrogen from itself. Because the cyclic transition state for this abstraction is most favorable when it contains six atoms, four-carbon butyl group branches are formed. The mechanism for the formation of these butyl branches is outlined in Figure 24.2.

These two branching processes decrease the regularity of the polyethylene macromolecules. Individual polymer chains may have long branches or butyl branches that occur at random positions. As we will see shortly, this irregularity in the structure dramatically affects the physical properties of the polymer.

❶ The radical carbon at the end of a growing polymer chain bends back and abstracts a hydrogen from the interior of the molecule. The most favorable size for the cyclic transition state is six atoms. This process is favorable because the original primary radical is converted to a more stable secondary radical.

❷ Polymerization can continue at the site of the new secondary radical.



❸ This results in a four-carbon branch on the ultimate macromolecule.

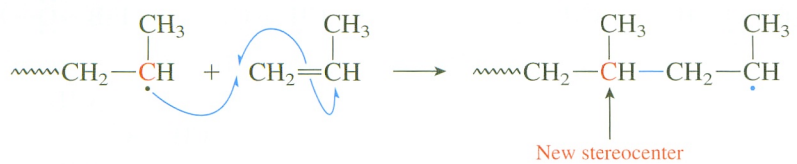
Active Figure 24.2 ORGANIC Chemistry Now™

MECHANISM OF THE FORMATION OF A BUTYL BRANCH DURING THE POLYMERIZATION OF ETHYLENE. Test yourself on the concepts in this figure at **OrganicChemistryNow.**

PROBLEM 24.4

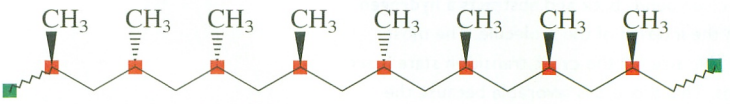
In addition to the four-carbon branches shown in Figure 24.2, polyethylene has a smaller number of branches containing three carbons. Show the steps in the mechanism for the formation of these three-carbon branches.

Another type of irregularity results if the vinyl monomer that is used to make an addition polymer has two different substituents on one end of the double bond. Propylene (propene), with a hydrogen and a methyl group on one of the vinyl carbons, provides an example. When such a monomer polymerizes, a new stereocenter (an asymmetric carbon chirality center) is created each time a new monomer is added:

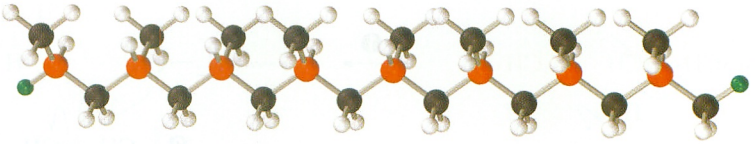


Because there is no preference for one absolute configuration over the other at this new stereocenter, the resulting macromolecule has a random configuration at its many ste-

reocenters and is termed **atactic.** A partial structure for atactic polystyrene is shown in the following diagram:

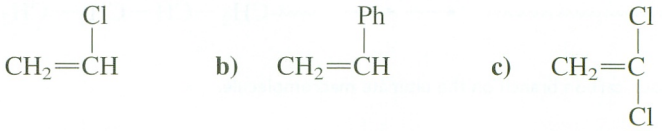


Atactic polypropylene
(random configuration at the carbons bonded to the methyl groups)



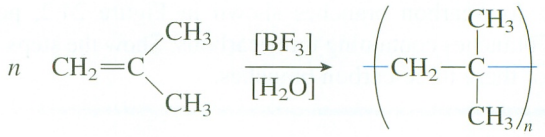
PROBLEM 24.5

Which of these monomers could form an atactic polymer?



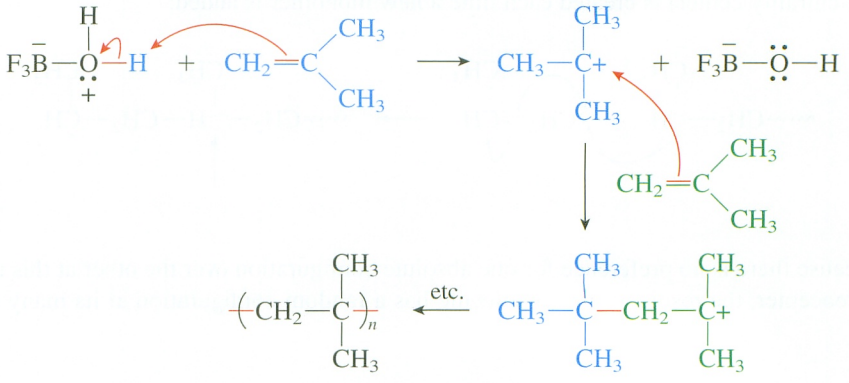
24.3 IONIC POLYMERIZATION

As well as mechanisms involving radical intermediates, addition polymers can be made by mechanisms involving cationic or anionic intermediates. For example, polyisobutylene is made by treating isobutylene with a small amount of boron trifluoride and water:



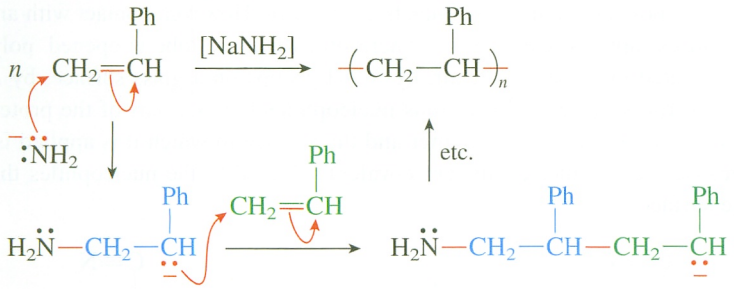
Isobutylene Polyisobutylene

The Lewis acid–base complex of water and boron trifluoride donates a proton to an isobutylene monomer to produce a carbocation. This carbocation adds to another isobutylene monomer to produce a larger carbocation, and the process continues, producing the polymer:

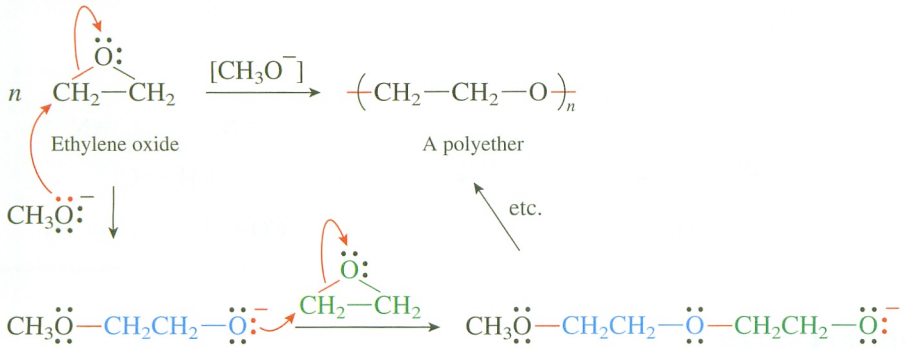


Because each addition occurs so as to form the more stable tertiary carbocation, the monomers are connected in a regular head-to-tail fashion. Cationic polymerization can be used only when one vinyl carbon of the monomer is substituted with groups that can stabilize the intermediate carbocation, as is the case with the two methyl groups of isobutylene.

Addition polymerization can also occur by a mechanism involving anionic intermediates. For example, styrene can be polymerized by the addition of a small amount of sodium amide. In this case the amide anion adds to the double bond to produce a carbanion. This carbanion then adds to another styrene molecule to form a larger carbanion, and the process continues to form polystyrene:



Most addition polymers are prepared from vinyl monomers. However, another type of addition polymer can be formed by ring-opening reactions. For example, the polymerization of ethylene oxide can be accomplished by treatment with a small amount of a nucleophile, such as methoxide ion. The product, a polyether, is formed by a mechanism involving anionic intermediates:

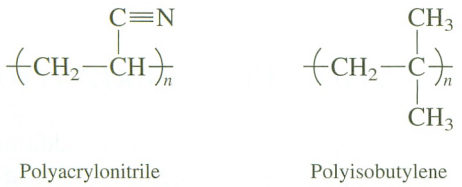


PROBLEM 24.6

Explain why polyethylene cannot be prepared by cationic polymerization whereas polystyrene can.

PROBLEM 24.7

Anionic polymerization is a good method for the preparation of polyacrylonitrile but not polyisobutylene. Explain.

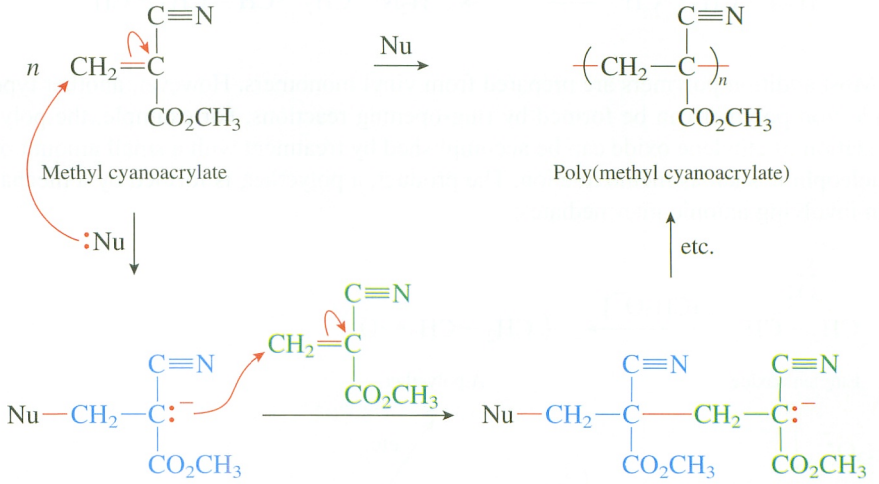


Polyacrylonitrile Polyisobutylene

Focus On

Super Glue

Super glue is a polymer of methyl cyanoacrylate. Because both the cyano and carbonyl groups of the monomer help stabilize carbanions, this compound is sensitive to polymerization by the anionic mechanism. The tube of glue contains very pure monomer, which does not polymerize until it contacts an initiator. However, contact with any nucleophile causes rapid polymerization. Therefore, when the tube is opened, polymerization is initiated by water in the air, by SiOH groups on a glass surface, by FeOH groups on an iron surface, or by various nucleophiles that are part of the proteins in skin. The adhesion between the polymer and the surface to which it is applied is very strong because the polymer chains are covalently linked to the nucleophiles that are part of the surface!



PROBLEM 24.8

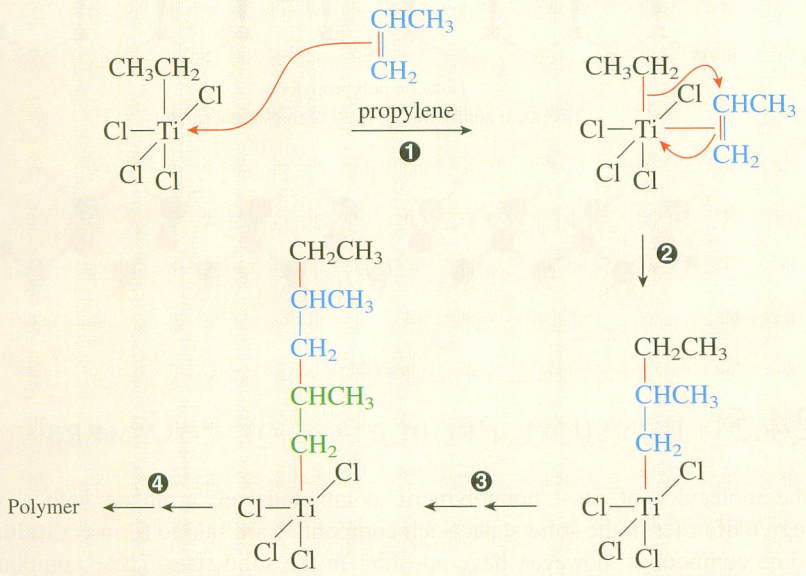
In contrast to the formation of a polyether from the reaction of ethylene oxide with a small amount of methoxide ion, a similar reaction using THF does not result in the formation of a polymer. Explain.

24.4 Coordination Polymerization

Perhaps the most important development in the area of addition polymerization was the discovery of a method for preparing vinyl polymers using metal catalysts. This breakthrough earned Karl Ziegler and Giulio Natta the 1963 Nobel Prize in chemistry

❶ The active catalytic species results from the transfer of an ethyl group from an aluminum to form a sigma bond to a titanium species. Propylene forms a "pi complex" with the titanium by interaction of its pi MOs with a vacant coordination site on the metal.

❷ The ethyl group migrates to one carbon of the double bond of the coordinated propylene, and the other carbon forms a sigma bond to the titanium. This creates a vacant coordination site on the metal, so the process can occur again.



❹ Continuation of this process produces polypropylene.

❸ The process of steps 1 and 2 is repeated as another propylene coordinates to the titanium, followed by migration of the new, larger alkyl group.

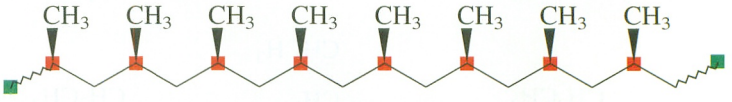
Figure 24.3

MECHANISM OF POLYMERIZATION INVOLVING A METAL COORDINATION CATALYST (SIMPLIFIED VERSION).

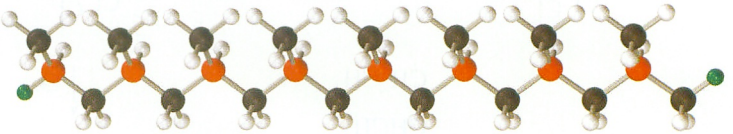
and is probably used today to produce a larger amount of vinyl polymers than all other methods combined. Although various catalysts have been used, a typical one uses an organometallic compound, such as triethylaluminum, and a transition metal halide, such as titanium tetrachloride. Although the mechanism is complex, a simplified version that has the correct general features is shown in Figure 24.3 for the polymerization of propylene. Basically, the mechanism proceeds by coordination of a monomer to a titanium that has an alkyl group sigma bonded to it. The alkyl group then migrates to one carbon of the double bond of the coordinated monomer while the other carbon forms a sigma bond to the titanium. This step regenerates the original catalyst, but with a larger alkyl group bonded to it. Additional monomer units are added in a similar fashion.

What makes the method using Ziegler-Natta catalysts so important? The resulting polymers are much more regular than those produced by other methods. For example, polyethylene produced by using a coordination catalyst is linear. It does not have the short or long branches that characterize polyethylene that is produced by a radical

initiator. Furthermore, coordination polymerization can be used to prepare stereoregular polymers. For example, polypropylene can be prepared with identical configuration at all of the stereocenters. The resulting **isotactic** polypropylene has very different, and much more useful, properties than the atactic polypropylene that is produced by radical polymerization. Let's see how the structure and regularity of these polymers affect their physical properties.



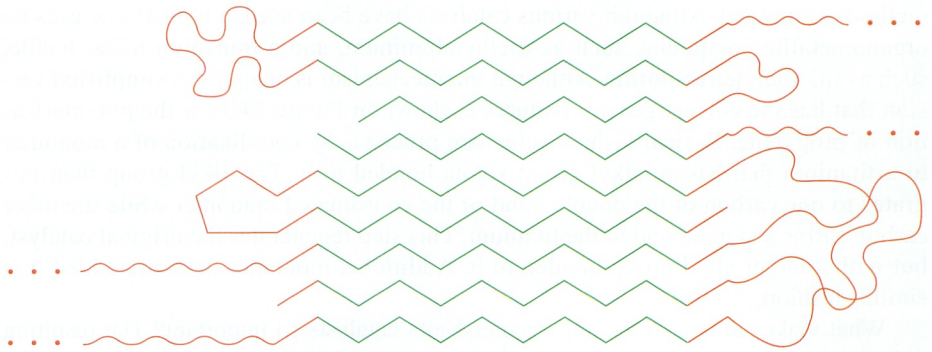
Isotactic polypropylene
(identical configuration at all of the stereocenters)



24.5 Physical Properties of Polymers

The molecules of most nonpolymeric compounds are arranged with a very high degree of order in the solid state. Such compounds are said to form **crystalline solids.** Some compounds, however, have no order in the solid state. These compounds form glassy solids with a random arrangement of molecules and are said to be **amorphous.**

The enormous molecules of a polymer such as polyethylene are too long to form a completely crystalline solid. However, many polymers are semicrystalline; that is, they have both crystalline and amorphous regions. For example, solid polyethylene has crystalline regions, called **crystallites,** where the chains are arranged in a very ordered manner, along with amorphous regions that are completely disordered. The part of a polyethylene molecule that is in a crystallite has an anti conformation about each of its carbon–carbon bonds. The resulting zigzag chain can pack well with the zigzag chains of other molecules. A two-dimensional picture of a crystallite can be represented schematically as shown in the following diagram:



These crystallites vary in size and shape and are much smaller than the crystals of a normal organic compound. An individual crystallite has dimensions on the order of 10^3 Å (100 nm). Recall that the length of most covalent bonds is slightly greater than 1 Å. Therefore, the ordered part of a crystallite extends over a region containing tens to hundreds of bonds. When a chain reaches the boundary of a crystallite, it may bend back and become part of the crystallite again. Other chains wander off into the amorphous region. Some of these remain in the amorphous region; others return to the same crystallite, and some even become part of another crystallite. In general, polymers that have more and larger crystalline regions are stiffer and stronger and are more useful for many applications.

Regularity in the structure of a polymer favors crystallinity because the chains can pack closer together. The head-to-tail bonding of the individual monomer units is one type of regularity that is present in most addition polymers. The presence of branches is an irregularity that decreases the ability of the polymer chain to pack into crystalline regions. Therefore, linear polyethylene prepared by polymerization using a Ziegler-Natta catalyst is more crystalline than the highly branched polyethylene produced by a radical mechanism. In addition, polymers must have a regular stereochemistry if they are to be crystalline. Atactic polymers are completely amorphous. Again, the ability to use coordination polymerization for the preparation of stereoregular polymers is extremely valuable.

Crystallinity is also favored by strong forces between polymer chains. In a nonpolar polymer such as polyethylene, the only forces holding the chains in place are van der Waals forces (see Section 2.5). Although these attractions are relatively weak, there are many of them, so their total force can be quite large. However, polymers with polar groups have stronger intermolecular forces and are more crystalline than nonpolar polymers, other factors being equal.

Most addition polymers are **thermoplastics;** that is, they are hard at room temperature but soften and eventually melt as they are heated. At low temperatures there is very little motion of the molecules and the polymer is glasslike and brittle. As the temperature of the polymer is raised, it passes through its glass transition temperature (T_g). Above T_g, more motion of the chains is possible and the polymer is a rubbery solid. Eventually, the polymer passes through its crystalline melting point (T_m) and melts to form a viscous liquid. Many semicrystalline polymers are most useful at temperatures between T_g and T_m. Both T_g and T_m increase as the crystallinity of the polymer increases and as the strength of the intermolecular forces between the polymer chains increases. The total intermolecular force increases as the length of the polymer chains increases.

In general, polymers have no useful mechanical properties until the chains reach a certain average length. Above this minimum length, the strength increases as the polymer gets longer, but it also becomes more difficult to process the polymer. Therefore, the average molecular mass is usually a compromise, large enough that the polymer has useful mechanical properties but not so large that it cannot be molded, extruded, or drawn into fibers.

PROBLEM 24.9

Explain which of these monomers produces the more crystalline polymer.

a) $CH_2{=}CH(Cl)$ or $CH_2{=}C(Cl)_2$ using radical polymerization

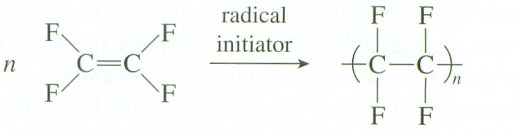
b) $CH_2{=}CH(CH_3)$ or $CH_2{=}CH(CO_2CH_3)$ using radical polymerization

c) $CH_2{=}CH(Ph)$ using radical polymerization or coordination polymerization

d) $CH_2{=}CH(CH_3)$ or $CH_2{=}C(CH_3)_2$ using radical polymerization

PROBLEM 24.10

Explain why Teflon is linear and has no stereochemical complications even though it is prepared by radical polymerization.



Tetrafluoroethylene — Poly(tetrafluoroethylene) (Teflon)

24.6 Major Thermoplastic Addition Polymers

Four thermoplastic addition polymers—polyethylene, poly(vinyl chloride), polypropylene, and polystyrene—comprise the majority of the total amount of polymers manufactured in the United States. In 2002 a total of 33.6 million metric tons of these plastics was produced, distributed as shown in Table 24.1.

Table 24.1 Output of Thermoplastic Polymers

Polymer	Structure	Amount (million metric tons)
Polyethylene	$-(CH_2-CH_2)_n-$	16.0
Poly(vinyl chloride)	$-(CH_2-CH(Cl))_n-$	6.9
Polypropylene	$-(CH_2-CH(CH_3))_n-$	7.7
Polystyrene	$-(CH_2-CH(Ph))_n-$	3.0

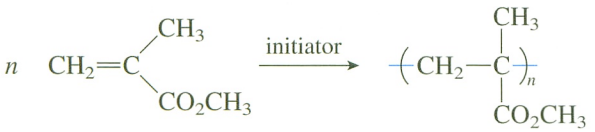
Two types of polyethylene are manufactured: high-density polyethylene (HDPE) and low-density polyethylene (LDPE). HDPE is produced by coordination polymerization using a Ziegler-Natta type catalyst. Its regularity and the absence of branches make it more crystalline, and the resulting closer packing of its chains results in a higher density. It is strong and rigid, with a higher T_m. It is used to make a variety of containers and plastic items, such as bottles, mixing bowls and other kitchen items, and toys. LDPE is produced by radical polymerization and has both long and short branches. As a result, it is more amorphous and less dense because its chains are not packed as closely. It is weaker and less rigid than HDPE. A majority of it is used as film in packaging products, such as garbage bags, household plastic wrap, and the transparent film used to cover trays of meat in the supermarket. Its major advantage is its low cost.

Poly(vinyl chloride), also known as PVC, is prepared by radical polymerization to produce material composed of an average of 10,000 to 24,000 monomer units. It is atactic and therefore amorphous, but it has a relatively high T_g because of the large size of its molecules and its polar carbon–chlorine bonds. It is a rigid material and is used to make pipe, panels, and molded objects. About 68% of PVC is used in the building and construction industry. A more flexible form of PVC is produced by adding a plasticizer such as dioctyl phthalate. This is used to prepare electric wire coatings, film, and simulated leather or "vinyl."

Polypropylene owes its current market success to the development of coordination polymerization. Before 1957 it was not produced commercially because radical polymerization gives an atactic polymer that is amorphous and has poor mechanical properties. Using a coordination catalyst, however, enables the production of an isotactic polymer that is semicrystalline. This material is stiff and hard and has a high tensile strength. Among its many useful products are rope, molded objects, and furniture.

Polystyrene is made by radical polymerization and is atactic and amorphous. Incorporation of small air bubbles produces a foam (Styrofoam) that finds a major use in packaging materials and insulation.

Many other addition polymers are manufactured commercially, although in much smaller amounts than those just described. For example, poly(methyl methacrylate) is prepared by radical polymerization of the methyl ester of methacrylic acid:



Methyl methacrylate Poly(methyl methacrylate)

Although it is atactic and amorphous, its polar groups cause it to have a relatively high T_g (110°C), and it is rigid and glasslike at normal temperatures. It is used to make products such as Plexiglas and Lucite.

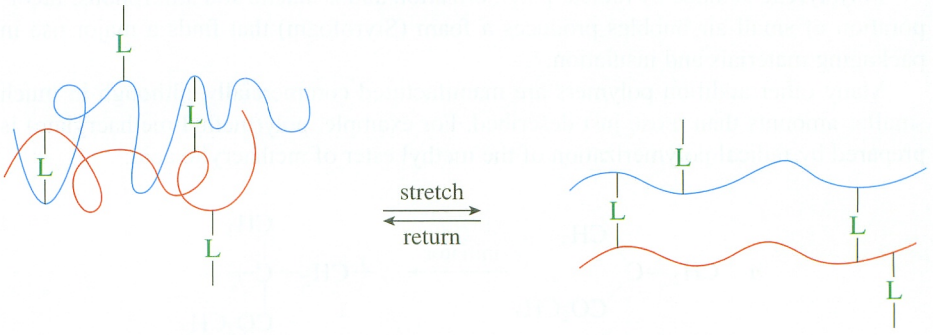
PROBLEM 24.11

Do you think that poly(methyl methacrylate) could be prepared by cationic polymerization? by anionic polymerization? Explain.

24.7 ELASTOMERS

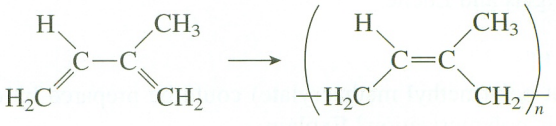
Several general requirements must be met for a polymer to be elastic—that is, to stretch under the application of force but return to its original shape when the force is released. The polymer should be predominantly amorphous so that its T_g is below room temperature. The individual molecules of an amorphous polymer are not in fully extended, anti conformations; instead, they have random, coiled conformations. When a force that pulls on opposite ends of the molecules is applied, the molecules assume an anti conformation about more bonds and thus they become longer; that is, they stretch. Although the stretching tends to arrange the molecules in extended, zigzag conformations that are favorable for crystallization, the overall shapes of the elastomer molecules are such that crystallization does not readily occur. Furthermore, most elastomers are nonpolar, so only weak attractive forces exist between chains. Therefore, when the force is removed, the molecules tend to return to their initial random conformations because these random shapes are favored by entropy (disorder).

In addition, however, it is necessary to somehow keep the chains from slipping past each other entirely as they are stretched. If this is not prevented, the material will simply pull apart rather than stretch and then return to its previous shape when the stretching force is removed. This is accomplished by the formation of **cross-links**—that is, groups that connect separate chains by covalent bonds. If only a few of these cross-links are present, then the molecules are still flexible enough to be stretched, but the cross-links prevent the molecules from separating entirely, and they return to their original shape when the stretching force is removed. The following diagram attempts to illustrate this process for a simplified system of only two polymer chains. In this picture, -L- is used to represent the cross-linking groups. A few cross-links couple the two chains while others connect them to other polymer molecules.



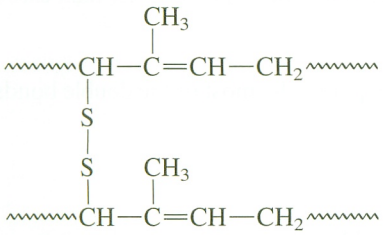
Random coil conformation Stretched conformation

Natural rubber can be viewed as a polymer formed by addition of isoprene monomers at the ends of the 1,3-diene units (although nature does not prepare it in this manner).



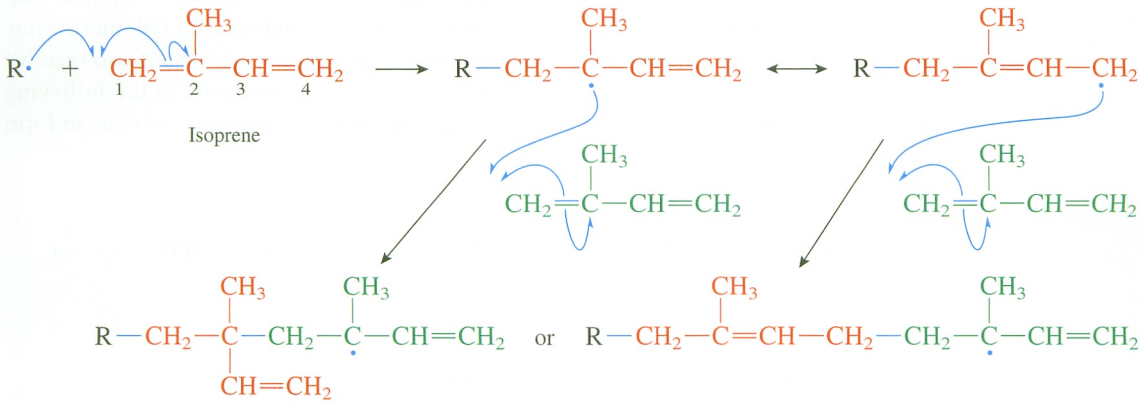
Isoprene Natural rubber

The double bonds of the rubber molecules all have the cis, or *Z*, configuration. This causes bends in the chains that make the molecules less able to crystallize. To prevent the molecules from slipping past each other when the rubber is stretched, the molecules are cross-linked by treatment with sulfur in a process called *vulcanization*. Although the exact details of vulcanization are not known, links between different chains are formed by one or two sulfur atoms:



A typical cross-link formed in vulcanization

Isoprene can be polymerized in the laboratory by a radical chain mechanism. As shown in the following equations, the odd electron of the initially produced radical is delocalized onto both C-2 and C-4 by resonance. Either of these carbons may add to another isoprene monomer to continue the chain reaction. If C-2 adds, the process is called 1,2-addition; if C-4 adds, the process is called 1,4-addition. (This is similar to the addition of electrophiles to conjugated dienes discussed in Section 11.13 and the addition of nucleophiles to α,β-unsaturated carbonyl compounds described in Section 18.10.)



Isoprene

1,2-Addition

1,4-Addition

Radical polymerization results mainly in 1,4-addition of the monomer units, and the double bonds are predominantly in the trans or *E* configuration. Because its trans double bonds allow its chains to crystallize more readily, this product, known as gutta percha, has a higher T_g than natural rubber and is hard and inelastic at room temperature. Recently, however, a method for the polymerization of isoprene using a coordination catalyst has been developed. The polymer results from 1,4-addition with almost all of its double bonds in the cis configuration and is nearly identical to natural rubber.

Synthetic rubbers now constitute about two thirds of the rubber that is used worldwide. The major synthetic rubber, called styrene-butadiene rubber, or SBR, is a copolymer formed by radical polymerization of a mixture of 25% styrene and 75% 1,3-butadiene. The monomers add in a random sequence. The incorporation of each

butadiene monomer occurs predominantly by 1,4-addition, and the double bond is usually trans. However, the random placement of the styrene units and their stereochemical disorder keep the rubber from being too crystalline. The product can be vulcanized in a manner similar to natural rubber and finds a major use in automobile tires.

PROBLEM 24.12

Explain why radicals prefer to add to carbon 1 of isoprene rather than carbons 2, 3, or 4.

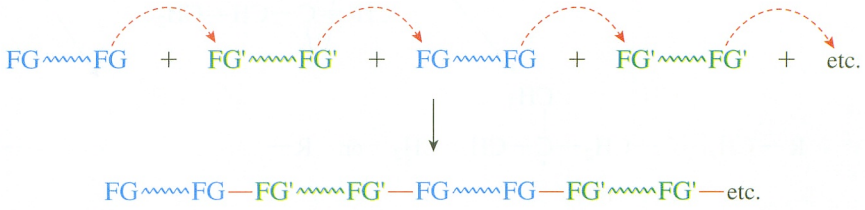
PROBLEM 24.13

Show a partial structure for SBR and explain why most of the double bonds have a trans configuration.

24.8 Condensation Polymers

Besides addition polymerization, the other general way to prepare polymers is known as **condensation polymerization** or **step growth polymerization.** Much of the pioneering work on condensation polymerization was conducted by Wallace Carothers while he was employed by DuPont. He recognized that many natural polymers are formed from monomers with two reactive functional groups. For example, proteins are polymers of amino acids, which contain both amine and carboxylic acid groups. The formation of amide bonds is used to connect one monomer to another. Carothers's attempts to imitate nature led to a whole industry based on condensation polymerization.

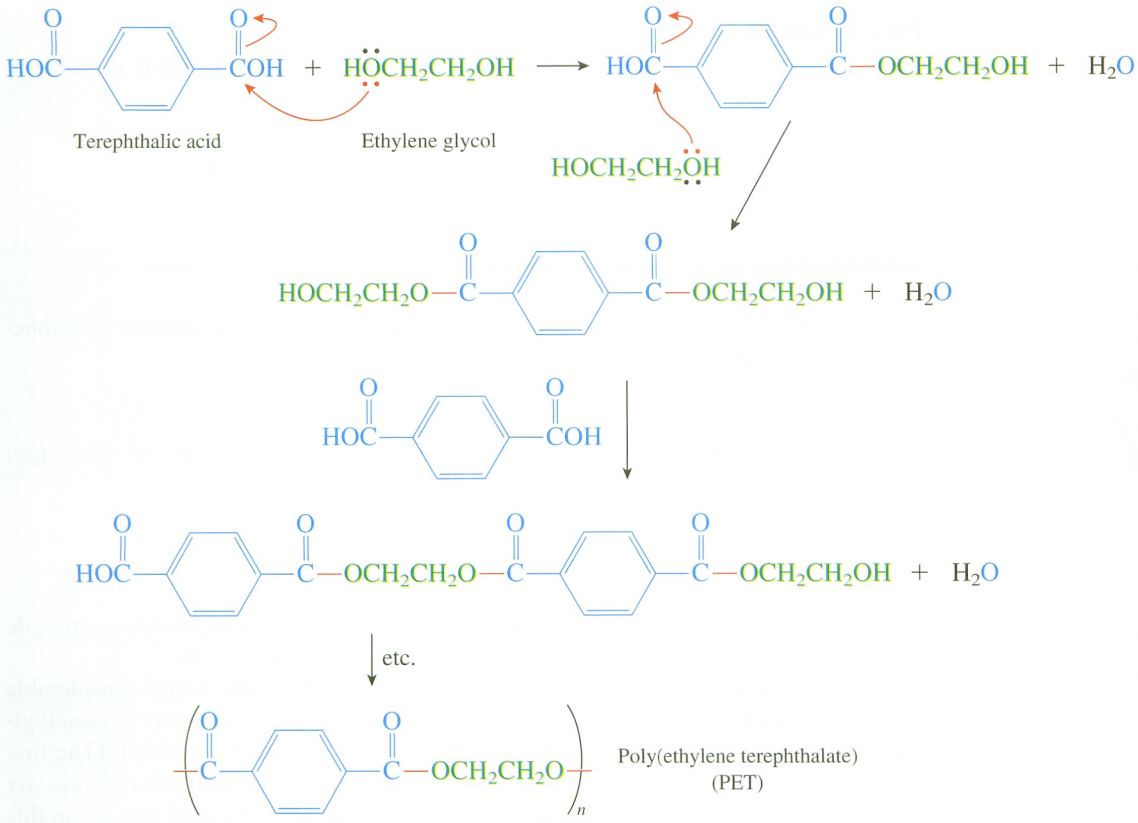
The key to the formation of a condensation polymer is the presence of two reactive functional groups in each monomer. This is illustrated schematically in the following equation, where FG and FG′ represent different functional groups that can react to form a covalent bond.



For example, the functional group represented by FG might be an amine, and the functional group represented by FG′ might be a carboxylic acid. Formation of an amide bond between the amine of one monomer and the carboxylic acid of the other results in the formation of a dimer. Continuation of this process results in polymer formation. Let's examine some specific examples to better understand how this process works.

One important group of condensation polymers is the polyesters. The most important commercial polyester is formed from the reaction of terephthalic acid (a diacid) with ethylene glycol (a diol). This polymerization occurs in a stepwise fashion (hence the name step growth polymerization). First, one carboxylic acid group of a diacid molecule and one hydroxy group of a diol molecule combine to form an ester, with the loss of water. Then a second diol molecule reacts with the unreacted carboxylic group on the other end of the diacid molecule, or a second diacid molecule reacts with the unreacted hydroxy group of the diol. Continuation of this process adds a new monomer unit at

each step, ultimately producing a polymer. The resulting polyester is called poly(ethylene terephthalate), or PET.



Because of the difficulty encountered in removing the water that is produced when an acid reacts with an alcohol, PET is produced commercially by the reaction of dimethyl terephthalate, the dimethyl ester of terephthalic acid, with ethylene glycol in an ester interchange reaction. The methanol that is formed in this reaction is readily removed by distillation.

PET has a high degree of crystallinity because it is linear and contains polar ester functional groups. It has a relatively high melting point (270°C). If the molten polymer is drawn through a small hole, fibers are formed. The drawing process extends and orients the molecules that form the fibers, maximizing the dipole–dipole interactions between chains and increasing their crystallinity. This results in a high tensile strength for the fiber. This fiber, known as Dacron or Terylene, is spun into thread that is used to make polyester fabrics or blended with cotton to make permanent press fabrics. PET is

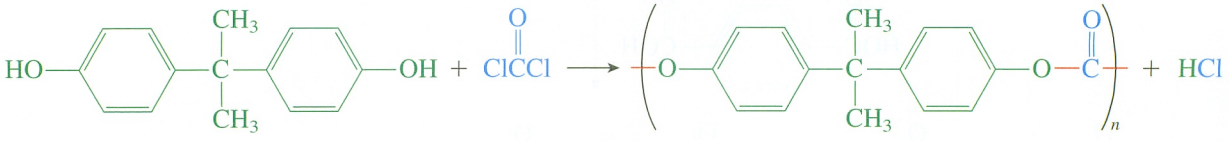
also used to make a strong film, called Mylar, and is the major plastic used to make bottles for soft drinks.

PROBLEM 24.14

Show the repeat unit of the polymer formed from adipic acid and ethylene glycol:

Adipic acid

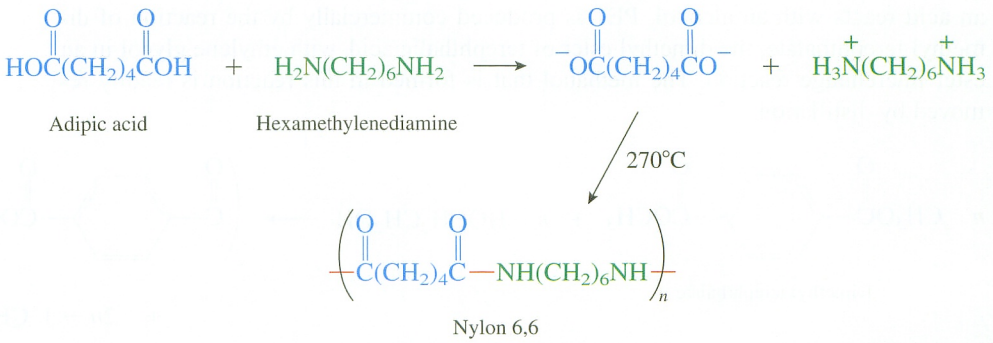
Another important polyester is the polycarbonate formed by the reaction of bisphenol A with phosgene:



Bisphenol A Phosgene A polycarbonate

The resulting polymer, known as Lexan, is useful because of its high-impact strength. It is used in products such as football helmets and motorcycle helmets.

Condensation polymers based on an amide linkage have also found considerable commercial applications. For example, when the salt of adipic acid and hexamethylenediamine is heated to 270°C, a polyamide known as nylon 6,6 is formed. (The first number in the name of the nylon designates the number of carbons in the diamine, six in this case, and the second designates number of carbons in the diacid, also six in this case, that are used to form the nylon.)



Adipic acid Hexamethylenediamine

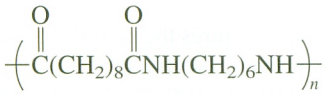
Nylon 6,6

This same polyamide can be prepared by reaction of the diacyl chloride of adipic acid with hexamethylenediamine. In Section 19.6 we saw that the conversion of the salt of a carboxylic acid and an amine to an amide could be accomplished by heating but that this method was not often used in the laboratory because of the rather vigorous conditions that must be employed. However, in an industrial setting, cost is a more important factor. Because the reaction starting only with the diacid and the diamine is much less expensive than first converting the diacid to its acyl chloride, the former method is the one used to prepare nylon 6,6.

Because of its polarity and its ability to form hydrogen bonds, nylon 6,6, along with other polyamides, has strong intermolecular forces. It has a high melting point (250°C) and can be drawn into fibers with good tensile strength. Nylon 6,6 was the first synthetic fiber. (In May 1940 the first pairs of nylon stockings went on sale. Within 4 days, nearly the entire stock of 4 million pairs had been sold.) It is also used to make molded objects.

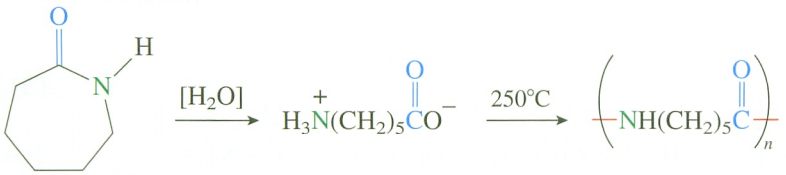
PROBLEM 24.15

Nylon 6,10 is quite rigid and is used in applications such as brush bristles. Show the monomers that are used to prepare this polymer.



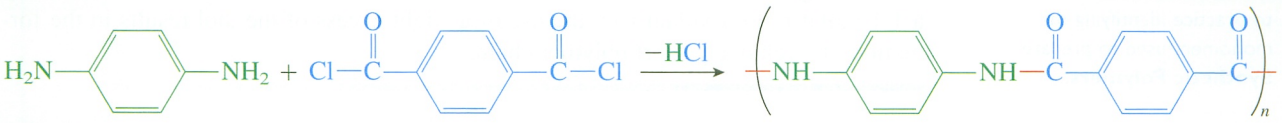
Other factors being equal, a polyamide has stronger intermolecular forces than a similar polyester because the polyester cannot form hydrogen bonds. As an illustration of this point, a polyester related to nylon 6,6—that is, one having only alkyl groups connecting the two hydroxy groups and the two carboxylic acid groups in its monomers—has weaker intramolecular forces and does not have useful mechanical properties. Changing to a more rigid diacid, such as terephthalic acid, increases the intramolecular forces and provides a more crystalline and more useful polyester.

Another polyamide is prepared by polymerization of ϵ-caprolactam. This monomer is different from the others that we have seen so far because it has two different functional groups in the same molecule. Therefore, only one type of monomer is needed to form the polymer. When the lactam is heated with a small amount of water, some is hydrolyzed to the amino acid, which forms an internal salt. Heating at 250°C causes formation of an amide bond while simultaneously regenerating water. Continuation of this process provides the polyamide known as nylon 6:



ϵ-Caprolactam Nylon 6

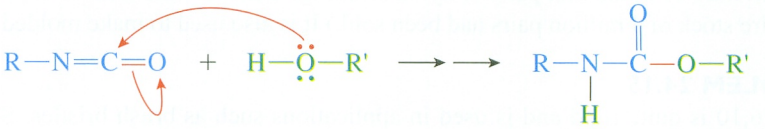
Use of a more rigid diamine and diacid derivative, such as 1,4-diaminobenzene and terephthaloyl chloride, provides a polyamide, known as Kevlar, with very interesting properties:



1,4-Diaminobenzene Terephthaloyl chloride Kevlar

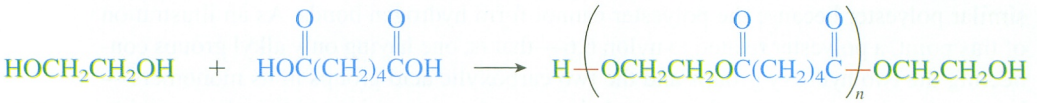
The rigid, rod-shaped molecules of Kevlar are very crystalline and can be used to form strong, stiff, high-strength fibers. Although this polymer is fairly expensive, it is used in high-tech applications such as bulletproof body armor.

Polyurethanes are produced by the reaction between alcohols and isocyanates. Isocyanates have a very reactive functional group that is subject to nucleophilic attack by an alcohol to give a carbamate or urethane:



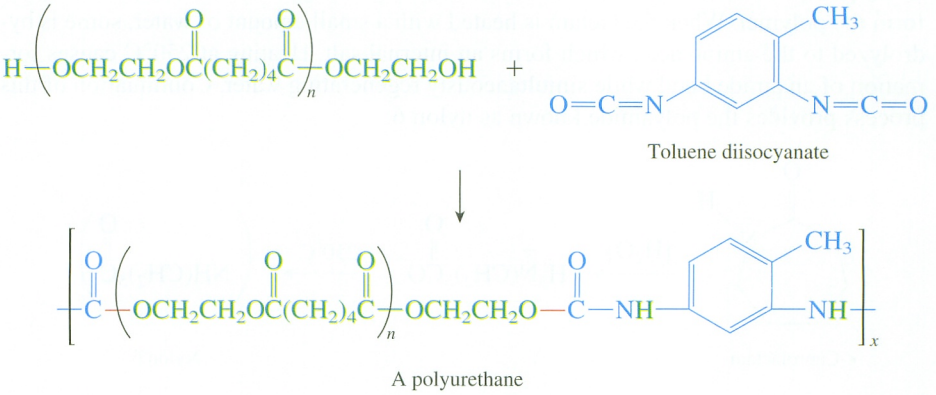
An isocyanate — A carbamate or urethane

Formation of a polyurethane, then, requires the reaction of a dialcohol with a diisocyanate. The dialcohol is often a small polymer, with a molecular mass of 1000 to 2000, that has hydroxy groups at each end. It is prepared by the reaction of a diacid, such as adipic acid, with a slight excess of a diol, such as ethylene glycol. Using a small excess of the diol ensures that the polymer chains are relatively short and have hydroxy groups at the ends:



Ethylene glycol (slight excess) — Adipic acid

This polymeric diol is then reacted with a diisocyanate, such as toluene diisocyanate, to produce the polyurethane:



Toluene diisocyanate

A polyurethane

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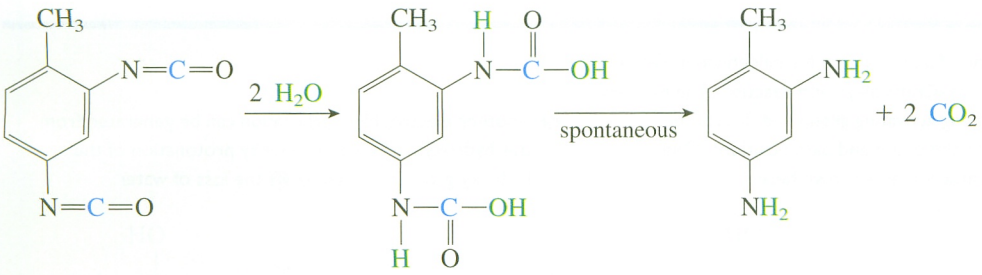
Click *Coached Tutorial Problems* to practice identifying the monomers used to prepare **Synthetic Polymers.**

PROBLEM 24.16

To form high-molecular-mass polyesters, the diol and the diacid must be used in exactly a 1:1 molar ratio. Explain why the use of a slight excess of the diol results in the formation of a relatively short polymer chain.

Polyurethane foams are prepared by including some water when the monomers are mixed. The reaction of an isocyanate with water produces a carbamic acid. As discussed in Section 23.4, a carbamic acid is unstable and spontaneously eliminates carbon dioxide to form an amine. This reaction is illustrated for toluene diisocyanate in the following equation:



A dicarbamic acid

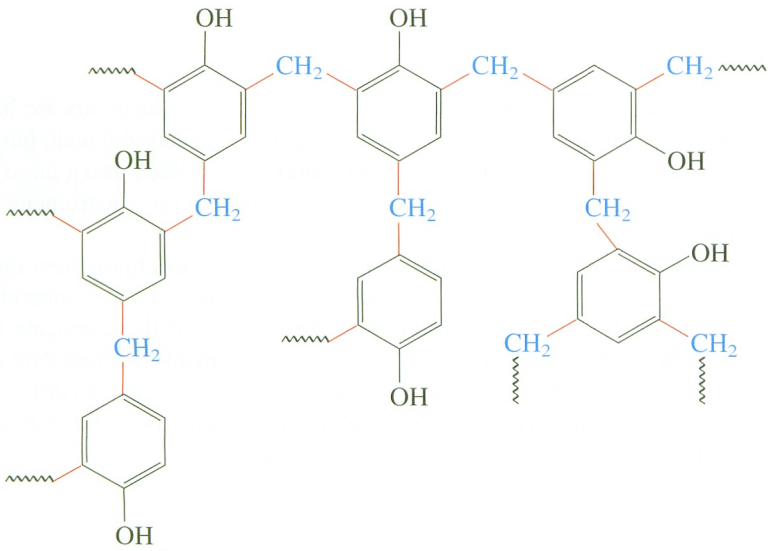
The carbon dioxide that is produced by the preceding equation is trapped in the polymer as it forms, resulting in a foamy polymer. Polyurethane foam is used to make cushions, pillows, and insulation.

24.9 THERMOSET POLYMERS

In contrast to the thermoplastic polymers that have been discussed so far, thermoset polymers do not soften or melt on heating. Instead, they become larger, harder, and more insoluble because cross-linking becomes very extensive. Essentially, the sample becomes one huge molecule as the polymer cures.

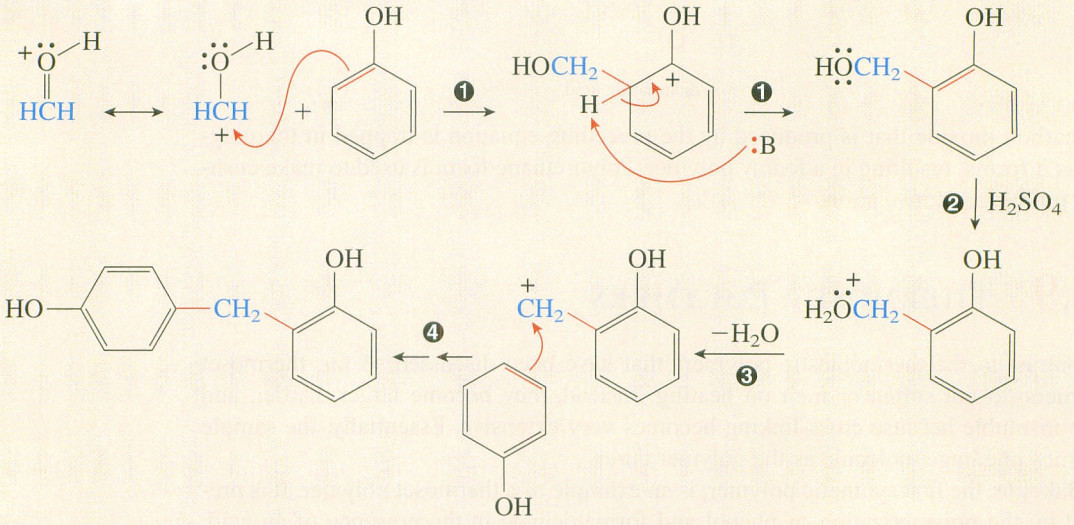
Bakelite, the first synthetic polymer, is an example of a thermoset polymer. It is prepared by the polymerization of phenol and formaldehyde in the presence of an acid. Carbocations produced by protonation of formaldehyde bond to the ortho and para positions of the highly reactive phenol molecules in a Friedel-Crafts alkylation reaction. The benzylic alcohols that are produced in this step react to produce carbocations that then alkylate additional phenol molecules. A mechanism for the first few steps of this polymerization process is shown in Figure 24.4.

Because each phenol has three sites (two ortho and a para) that can be linked by CH_2 groups, the resulting polymer is highly cross-linked. The structure of a part of the polymer can be illustrated as shown in the following diagram:



❶ The electrophilic carbon of a protonated formaldehyde molecule adds to phenol in a Friedel-Crafts alkylation reaction. The hydroxy group of phenol is a strong activating group and directs the incoming electrophile to the ortho and para positions. One possibility is the ortho attack that is shown here.

❷ Another electrophilic carbocation can be generated from this hydroxymethylated phenol by protonation of the hydroxy group followed by ❸ the loss of water.



Each phenol nucleus in this molecule has two additional reactive sites (the other ortho and/or para positions) where connections to other phenols can occur by this same mechanism. Ultimately, a highly cross-linked polymer is formed.

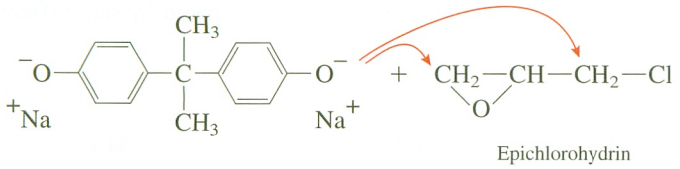
❹ The resulting carbocation can alkylate another phenol molecule. Again the new bond can be formed at the ortho or para position.

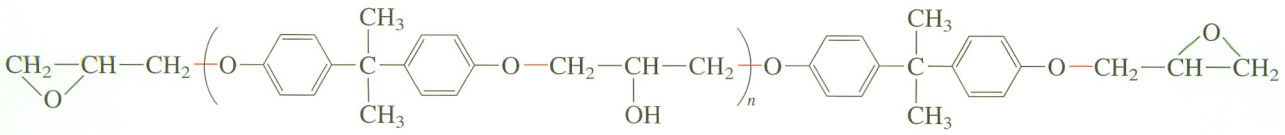
Figure 24.4

PARTIAL MECHANISM OF THE POLYMERIZATION OF PHENOL AND FORMALDEHYDE.

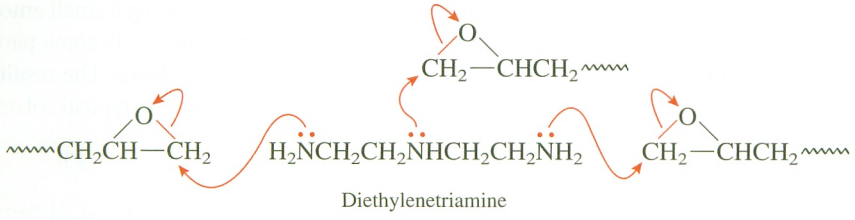
Some of the phenol units are linked at all three positions, whereas others are linked at only two. Because of its high degree of cross-linking, Bakelite does not melt, burns only with difficulty, and is an excellent electrical insulator. It is molded into a large variety of objects, including billiard balls, automobile distributor caps, instrument control knobs, and handles for cookware and toasters.

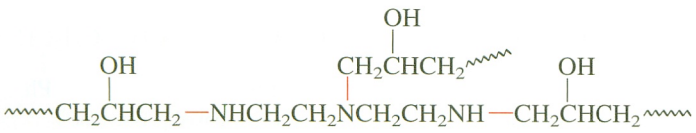
Epoxy resins, which are used as adhesives, are also thermoset polymers that form by cross-linking when the two components of the resin are mixed. One component is a low-molecular-mass linear polymer formed by the reaction of the conjugate base of bisphenol A with epichlorohydrin. The nucleophilic oxygens of the phenolate dianion can either displace the chlorine or open the epoxide ring of epichlorohydrin. A slight excess of epichlorohydrin is used to keep these polymer chains short and to ensure that the linear molecules have epoxide groups at their ends.





The second component of the glue is composed of a trifunctional amine such as diethylenetriamine. When the two components are mixed, the three nucleophilic nitrogens of the triamine react with the epoxide groups to form a highly cross-linked polymer, as shown in the following equation:



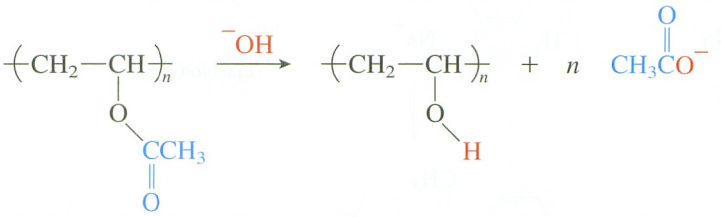


The reaction is complete in a few hours, and the polymer hardens to a strong adhesive.

24.10 Chemical Properties of Polymers

Although polymer molecules are enormous in comparison to the other molecules that we have discussed, their chemical reactions are nearly identical to those of

smaller molecules. For example, poly(vinyl alcohol) is prepared by saponification of poly(vinyl acetate):

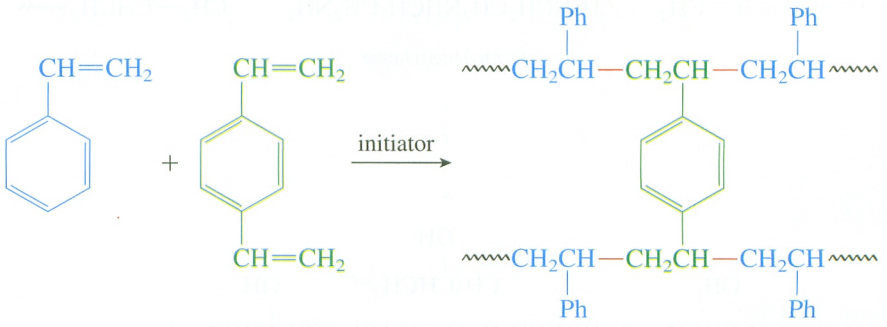


Poly(vinyl acetate) Poly(vinyl alcohol)

PROBLEM 24.17

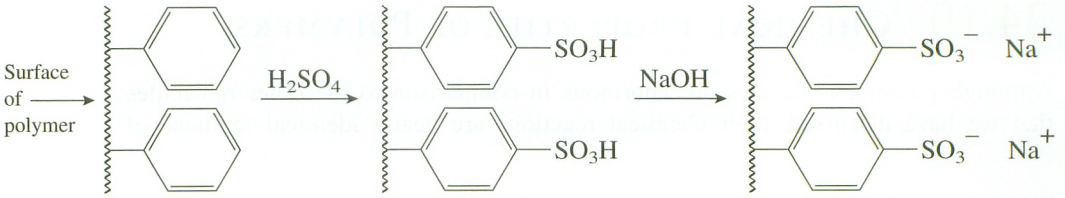
Explain why poly(vinyl alcohol) cannot be prepared by a direct polymerization reaction. (*Hint:* Draw the structure of the monomer that would be required.)

As another example, let's consider the chemical reactions that are used to prepare ion exchange resins. These resins are composed of small polymer beads that can be used to exchange one ion for another in aqueous solutions. The polymer that is used in these applications is a cross-linked polystyrene. To make this material, styrene containing a small amount of divinylbenzene is polymerized. Each vinyl group of divinylbenzene can become part of a separate polymer chain, so these groups act as cross-links between chains. The resulting polymer is used in the form of small beads that are completely insoluble in typical solvents.



Styrene 98% Divinylbenzene 2% Cross-linked polystyrene

The phenyl groups that are on the surface of these beads are accessible to added reagents and react like other aromatic compounds. (Of course, the phenyl groups in the interior of the bead do not usually react because the reagents are seldom able to penetrate the bead and reach them.) For example, the phenyl groups on the surface can be sulfonated by reaction with concentrated sulfuric acid (see Section 17.6).

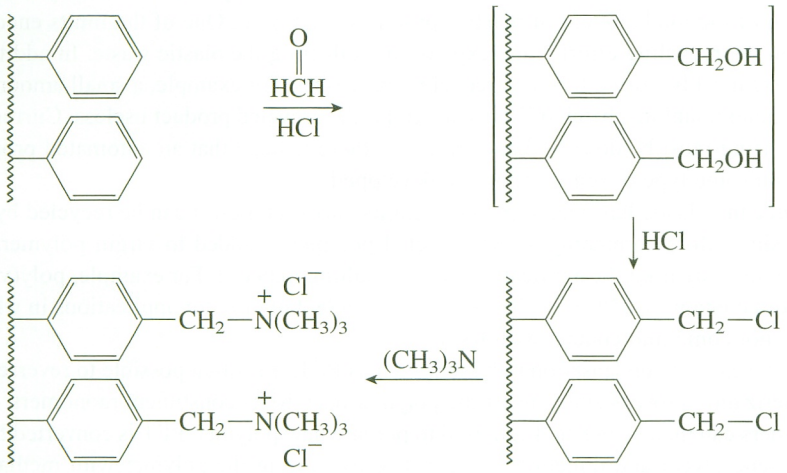


A cation exchange resin

The sulfonated polystyrene beads can be used as a cation exchange resin. For example, if the sulfonated resin is treated with sodium hydroxide, the sodium salt of each of the sulfonic acid groups is formed. This resin can then be employed to exchange sodium cations for other cations in an aqueous solution.

One application of such a cation exchange resin is to prepare soft water for cleaning purposes. Recall from the Focus On box "Synthetic Detergents BHT and BHA" on page 694 that hard water contains ions such as Ca^{2+} and Mg^{2+} that combine with soap molecules to produce a scummy precipitate. If hard water is passed through a cylinder containing the sodium form of an ion exchange resin, Na^+ ions are exchanged for the Ca^{2+} and Mg^{2+} ions. Although the total ionic charge in the water is unchanged, the soft water contains only sodium cations and no longer causes soap molecules to precipitate. After most of the sodium ions in the resin have been used to exchange for the cations in the water, the resin is regenerated by backflushing with a sodium chloride solution to replace the cations with Na^+.

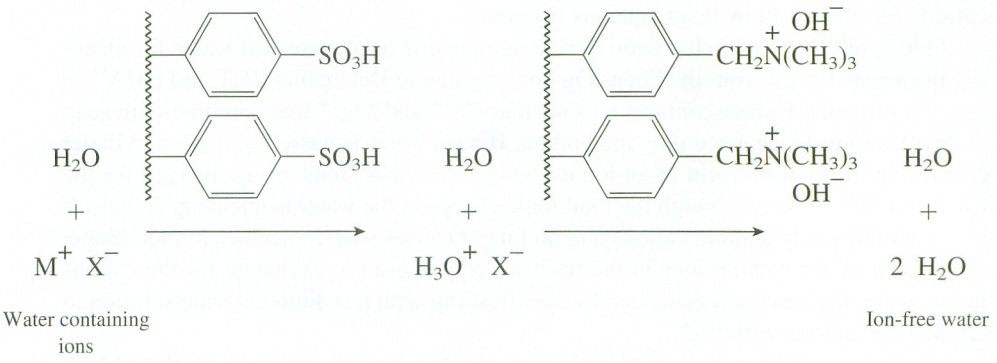
Note that a cation exchange resin has anionic groups attached to the phenyl groups of the polymer. The cations associated with these immobile anions can then be exchanged for other cations. To prepare an anion exchange resin, cationic groups must be attached to the phenyl groups of the resin. This is accomplished by reacting the cross-linked polystyrene with formaldehyde and hydrogen chloride. This first adds hydroxymethyl groups to the phenyl groups by the same mechanism shown in Figure 24.4. Then the hydroxy groups are replaced by chloride in a nucleophilic substitution reaction (see Section 10.5). Finally, the chloromethylated polystyrene is reacted with trimethylamine. This nucleophilic substitution reaction (see Section 10.6) produces a quaternary ammonium salt with an immobile cation and an exchangeable anion, an anion exchange resin.



An anion exchange resin

A combination of a cation exchange resin and an anion exchange resin is used to deionize water. First the water is passed through a cation exchange resin in its acidic form. This exchanges all of the cations in the water for H_3O^+. Then the water is passed through an anion exchange resin in its basic form. This exchanges all of the anions for OH^-, which reacts with the H_3O^+ to form water. On passing through both resins, all of

the ions in the water have been removed! This process is represented schematically in the following diagram:



Focus On

Recycling Plastics

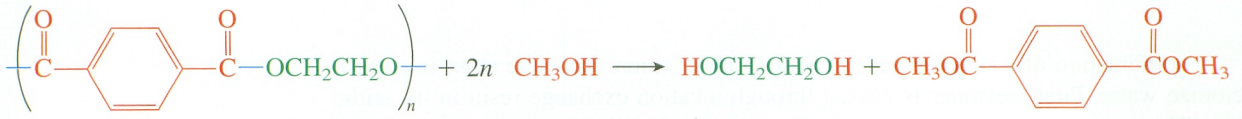
Courtesy of OrcaBoard

A bench made from recycled plastic.

As people have become more environmentally conscious, the need to recycle many of the materials, such as plastics, that are used in everyday life has been recognized. Although several billion pounds of plastics are currently recycled, this is only a small fraction of the total amount of plastics produced each year. One of the limits encountered in the recycling effort is the expense in collecting the plastic waste. In addition, the waste must be sorted for most recycling processes. For example, a small amount of PVC contaminant in a batch of PET can render the recycled product useless. Currently, such sorting must be done by hand, although there is hope that an automated process based on some type of sensor might be developed.

Once the plastic has been separated into its various types, it can be recycled by reprocessing. More commonly, some recycled polymer is added to virgin polymer, although this may limit the application of the resulting material. For example, poly(vinyl chloride) containing 25% recycled resin is available, but only for applications in which it does not come into contact with food.

In the case of condensation polymers such as PET, it is often possible to reverse the polymerization process and convert the polymer back to its constituent monomers. The monomers can then be purified and used to prepare new polymer. PET is converted back to ethylene glycol and dimethyl terephthalate by heating the polymer with methanol. This is exactly the reverse of the reaction that is used to prepare the polyester:



Unfortunately, there is no apparent way to accomplish the same thing with addition polymers. No one has yet figured out a way to convert polyethylene back to ethylene

or polystyrene back to styrene. However, a method has been developed to pyrolyze plastic waste to a chemical feedstock in a process that can be likened to the cracking process that is used in crude oil refining. Although much of the value that was added to the polymer in the manufacturing process is lost, this method has the distinct advantage that a mixture of various plastics can be used.

Finally, there is the option of burning the plastic for fuel. Although much of the value of the plastic is wasted, at least the energy content is recovered. Again, a mixture of various polymers can be used, although there is some concern about burning poly(vinyl chloride) because of its chlorine content.

Review of Mastery Goals

After completing this chapter, you should be able to:

- Show the repeat unit for any addition or condensation polymer. (Problems 24.18 and 24.19)
- Write the mechanisms for the formation of addition polymers that are prepared by radical, anionic, or cationic initiation. (Problems 24.20, 24.21, 24.22, 24.26, 24.28, 24.29, 24.30, and 24.32)
- Discuss the structure and stereochemistry of polymers in terms of both regular and irregular features. (Problems 24.24 and 24.35)
- Discuss how the physical properties of a polymer are related to its structure. (Problem 24.27)
- Discuss the chemical properties of a polymer. (Problem 24.31)

ORGANIC Chemistry Now™
Click *Mastery Goal Quiz* to test how well you have met these goals.

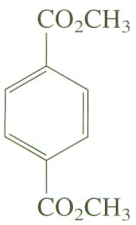
Additional Problems

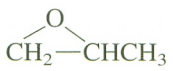
ORGANIC Chemistry Now™
Assess your understanding of this chapter's topics with additional quizzing and conceptual-based problems at **http://now.brookscole.com/hornback2**

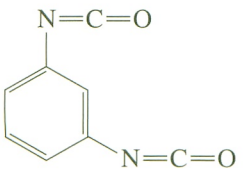
24.18 Show structures for the polymers that could be formed from these monomers and suggest the best method to accomplish each polymerization:

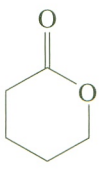
a) $NH_2(CH_2)_6NH_2$ + $HOC(CH_2)_8COH$ (O, O)

b) $CH_2{=}CH$ with CNH_2 (O)

c) $HO(CH_2)_4OH$ + 

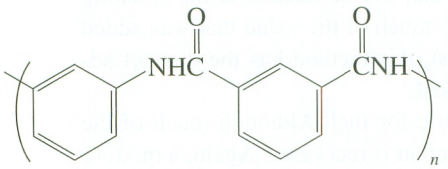
d) 

e) $HO(CH_2)_4OH$ + 

f) 

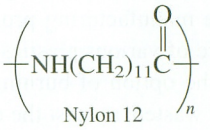
24.19 Show the monomers that could be used to prepare each of these polymers:

a)



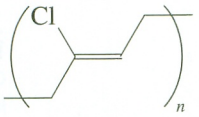
Nomex

b)



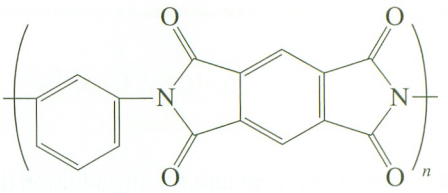
Nylon 12

c)

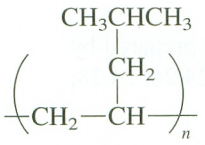


Neoprene

d)



e)



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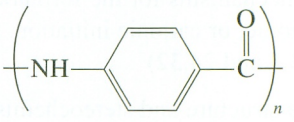
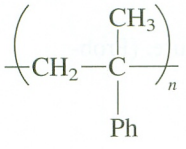
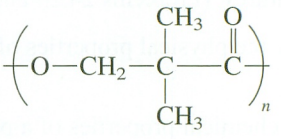


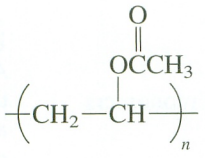
g)



h)

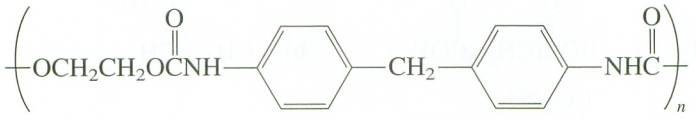


i)

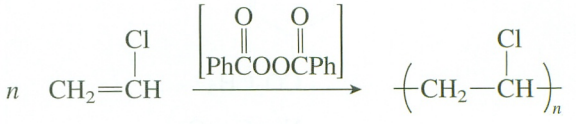


Poly(vinyl acetate)

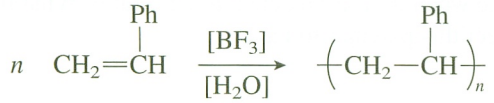
j)



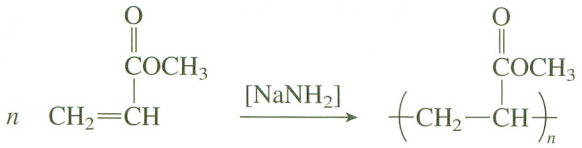
24.20 Show all of the steps in the mechanism for this reaction:



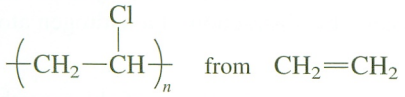
24.21 Show all of the steps in the mechanism for this reaction:

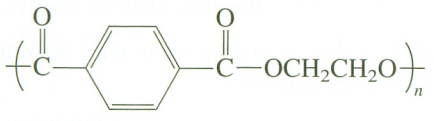
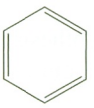


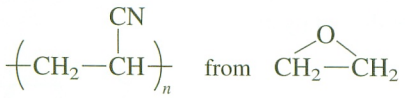
24.22 Show all of the steps in the mechanism for this reaction:



24.23 Show how these polymers could be prepared from the indicated starting materials. More than one step is needed.

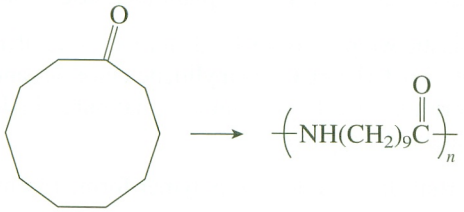
a)  from $CH_2{=}CH_2$

b)  from  and $CH_2{=}CH_2$

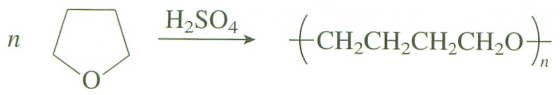
c)  from

24.24 Show the steps in the mechanism for the formation of a long-chain branch in the polymerization of styrene.

24.25 Show a synthesis of nylon 10 starting from cyclodecanone:

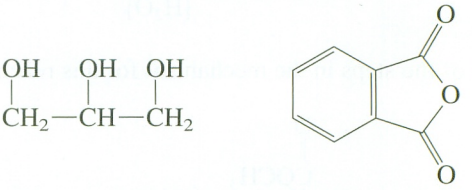


24.26 Although poly(butylene oxide) cannot be made by anionic polymerization of THF, it can be made by treating THF with acid. Suggest a mechanism for this process.



THF Poly(butylene oxide)

24.27 Show a partial structure for the polymer formed from glycerol and phthalic anhydride when they are reacted in a 2:3 ratio. What physical properties do you expect this polymer to have?



Glycerol Phthalic anhydride

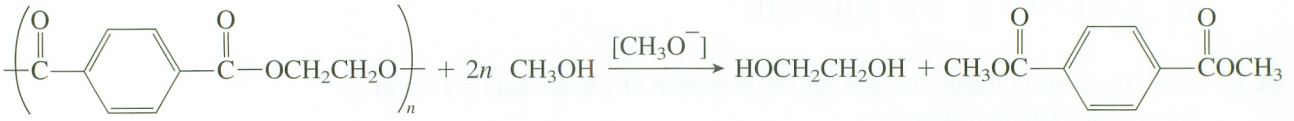
24.28 Explain why a small amount of BHT (butylated hydroxytoluene) is often added to styrene before it is sold for use in a research laboratory.

24.29 Show the ends of a molecule of polyethylene whose polymerization is initiated by $(PhCO_2)_2$ and terminated by abstraction of a hydrogen atom from another chain.

24.30 Show the steps in the mechanism for the formation of chloromethylated polystyrene by the reaction of polystyrene with formaldehyde and HCl.

24.31 Show a synthesis of an anion exchange resin starting with benzene and any other compounds with six or fewer carbons.

24.32 Show the steps in the mechanism for the conversion of PET back to its monomers using methoxide ion as the catalyst:



24.33 Contrary to intuition, a rubber band actually shortens when heated. Use the equation $\Delta G = \Delta H - T\Delta S$ to explain this observation.

24.34 Saran, a plastic wrap used for food storage, is a polymer prepared from a mixture of 85% $CH_2{=}CCl_2$ (vinylidene chloride) and 15% $CH_2{=}CHCl$ (vinyl chloride). Why do you suppose that pure vinylidene chloride is not used to make this polymer?

24.35 Show a partial structure for the polymer formed from 1,3-butadiene by radical polymerization. Discuss the possible structural variations in this polymer.

24.36 The crystallinity of polyethylene prepared by coordination polymerization can be decreased in a controlled fashion by the addition of a small amount of another alkene, such as 1-pentene. Show the structure of the resulting polymer and explain why its crystallinity is reduced.

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